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- (54) PURIFICATION OF ZINC SULPHATE SOLUTIONS
ELECTROLYTIC ZINC COMPANY OF AUSTRALASIA LIMITED
- | | | | | |
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| | 85025/75 | 499355 | C22B 15/12, 23/04 | |
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(57) Purifying Zn SO₄ solution to precipitate Cu, Cd, Co and Ni by (1) precipitating Cu and then (2) adding 1-6g/l of Zn dust in the added Sb at the temperature of 65° to boiling point of solution to precipitate Cd, Co and Ni.

Claim

1. A method of purifying zinc sulphate solutions from an electrolytic zinc plant to precipitate the impurities copper, cadmium, cobalt and nickel by a two-stage procedure consisting of the following stages:

Stage 1: Treatment of the said solution to precipitate copper using at least one procedure drawn from the group consisting of cementation with zinc dust, cementation with metallic iron, cementation with steel, precipitation as a copper sulphide, precipitation as a basic salt, solvent extraction and ion exchange.

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Stage 2: Addition of zinc dust to the copper depleted solution in the range 1 to 6 grams of zinc dust per litre of solution, in the presence of cadmium and added antimony to precipitate cadmium, cobalt and nickel from the said solution at a temperature from 65°C to the boiling point of the solution at atmospheric pressure, the resultant cementate being then separated from the then purified solution.

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TO BE COMPLETED BY APPLICANT

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Complete Specification for the invention entitled:

"A PROCESS FOR THE PURIFICATION OF ZINC SULPHATE SOLUTIONS"

The following statement is a full description of this invention, including the best method of performing it known to me:—

This document contains the amendments made under Section 43 and is correct for printing.

We certify that this and the following pages are a true and correct copy of the original Specification.

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This invention relates to the removal of impurities from aqueous zinc sulphate solutions.

More particularly, the invention concerns the removal of the metallic impurities copper, cadmium, cobalt and nickel from an aqueous zinc sulphate solution such as that generated in an electrolytic zinc plant prior to electrolysis for the recovery of zinc.

The invention provides a method of purifying zinc sulphate solutions from an electrolytic zinc plant to precipitate the impurities copper, cadmium, cobalt and nickel by a two-stage procedure consisting of the following stages:

Stage 1: Treatment of the said solution to precipitate copper using at least one procedure drawn from the group consisting of cementation with zinc dust, cementation with metallic iron, cementation with steel, precipitation as a copper sulphide, precipitation as a basic salt, solvent extraction and ion exchange, the temperature in this stage preferably being maintained between 75 and 95°C;

Stage 2: Addition of zinc dust to the copper depleted solution in the range 1 to 6 grams of zinc dust per litre of solution, in the presence of cadmium and added antimony to precipitate cadmium, cobalt and nickel from the said



solution at a temperature from 65°C to the boiling point of the solution at atmospheric pressure, preferably between 70 and 90°C, the resultant cementate being then separated from the then purified solution.

The temperature of the pulp within the second stage is preferably lowered from between 70 and 90°C to less than 65°C before the subsequent solid liquid separation step.

In a preferred embodiment of the invention the amount of zinc dust added in the first stage is within the range 75% to 150%, preferably 110 to 130% of the stoichiometric requirement to precipitate the copper in the zinc sulphate solution. The cementate resulting from the first stage may be separated from the copper depleted solution.

Stage 1 need not immediately precede Stage 2. The two stages may be separated by at least one other process step.

In further preferred embodiments of the invention, antimony may be added to the second stage in a quantity of between 0.5 and 10 mg antimony per litre of zinc sulphate solution.



The antimony which is added to the second stage according to the above preferred embodiment may be drawn from the group: a water-soluble antimony compound, Sb_2O_3 , Sb_2S_3 , antimony metal, antimony alloyed with the
5 zinc dust.

In the second stage, the lead is preferably present primarily as an alloy with the zinc dust used. the lead content of the zinc dust being in the range 0.1% to 2.0%. The lead may be added as a lead salt to the
10 zinc sulphate solution entering stage 2, the quantity of lead salt added being equivalent to 20 to 100 mg of lead per litre of solution.

Zinc dust may be added to the second stage at two separate points.

15 Elemental sulphur may be added to the second stage in a quantity of from 100 mg to 5 g of elemental sulphur per litre of zinc sulphate solution.

Spent electrolyte may also be added to the second stage.

20 Additional cadmium, preferably less than 5 g of cadmium per litre of zinc sulphate solution, may be added to the second stage, for example in one of the following forms: a water-soluble cadmium compound, a zinc sulphate solution containing cadmium, cadmium metal, an alloy with
25 zinc dust.



~~0.1% to 2.0% lead~~

- * additional cadmium is added to the second stage in one of the following forms : a water-soluble cadmium compound, a zinc sulphate solution containing cadmium, cadmium metal, an alloy with zinc dust
- * the quantity of additional cadmium added according to the above preferred embodiment is less than 5 g of cadmium per litre of zinc sulphate solution
- * at least one of the reactions herein referred to is performed in a batchwise fashion
- * at least one of the reactions herein referred to is performed in a continuous fashion
- * at least one of the cementation reactions is carried out in a counter-current manner.

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BACKGROUND OF THE INVENTION

The first step in the roast-leach-electrolysis route for recovery of zinc from sulphide concentrates is an oxidative roast to convert the zinc sulphide to impure zinc oxide and the sulphidic sulphur to sulphur dioxide.

20 The impure zinc oxide from the roasting step is subsequently leached in a dilute sulphuric acid solution, such as spent electrolyte solution recycled from the electrolysis step, to generate an impure zinc sulphate solution and a ferritic residue. In order to recover high grade zinc from a zinc sulphate solution and to carry out the electrolysis

25 efficiently, the zinc sulphate solution must be of a very high purity. Accordingly, removal of impurities from the



impure zinc sulphate solution is of the utmost importance. Iron, which is dissolved during the leaching process, may be selectively removed as a basic salt by careful adjustment of acidity, and impurities such as arsenic, antimony and silica may be removed at the same time by co-precipitating and/or absorption. However, other impurities such as copper, cadmium, cobalt and nickel remain in solution and must be precipitated and removed by additional means. A common method of removing these impurities is by precipitation with zinc dust or zinc powder, hereinafter referred to as cementation. Theoretically, all impurities which are more electro-positive than zinc can be removed in this way. The resulting product is herein referred to as cementate.

It is well known that cobalt is the most difficult impurity to remove by cementation on zinc dust from impure zinc sulphate solution and the prior art discloses several processes. Most of these are based on the observation that cementation of cobalt and also nickel is facilitated by the addition of activating elements, notably arsenic and antimony.

Normally arsenic is only an effective activating agent for cobalt removal if copper is present in solution (see British Patent 126,296). In practice, a copper concentration of approximately 200 mg/l is required to obtain the best result and the optimum quantity of arsenic, which is usually added to the solution as As_2O_3 , is frequently 50 - 200 mg/l. At the same time a high temperature

of $> 90^{\circ}\text{C}$ is required for satisfactory cobalt removal.

As a consequence a copper rich cementate is produced which is seriously contaminated with arsenic, an element which poses serious environmental problems when the copper residue is treated for copper recovery in copper smelting plants.

Recently two processes have been devised to overcome these problems. These include US Patent No. 4,049,514 which discloses a process for recovering arsenic from the copper residue by leaching in caustic soda followed by precipitation and recycling of the arsenic as copper arsenate.

Australian Patent 499,355 shows that the presence of copper is not essential for the removal of cobalt and nickel provided that large quantities of arsenic are added and the cementation is conducted in the presence of preformed cementate, preferably at a level of 30 - 50 g/l. The preformed cementate may be present either as a bed of settled solids remaining after decantation of the purified solution in batch operation, or as recycled solids in continuous operation.

Examples quoted in Australian Patent 499,355 reveal that the quantity of As_2O_3 added to the impure solution ranges from 100 to 250 mg/l, as a consequence of which the arsenic content of the cobalt/nickel rich precipitate is high, for example 38% and approximately 45% respectively in two of the quoted examples.

It is also pertinent to note that in the

quoted examples, although the cadmium content of the impure solution treated was 300 mg/l, the cadmium content of the cementate was in the range 0.1 to 0.2% i.e. an insignificant amount of cadmium is co-precipitated with the nickel and cobalt. Thus, in a commercial application of the process disclosed in Australian Patent 499,355 a three stage procedure is required. The first stage involves precipitation of copper with zinc dust followed by a second stage in which cobalt and nickel are cemented with zinc dust in the presence of large quantities of dissolved arsenic and of recycled preformed cementate. Finally, a third stage is required to remove cadmium.

Although processes for the retreatment of the arsenic-rich second stage cementate have been published (for example, Australian Patent Application 41903/78) to the best of the applicant's knowledge no commercial plant utilising these processes is currently operating. Thus, although the process disclosed in Australian Patent 499,355 overcomes some of the previously noted problems associated with the recovery of high grade copper residue it still requires the presence of a high concentration of arsenic, an element which has recently been claimed to be carcinogenic, and which is very dangerous to use in a commercial plant because of the probable formation of highly poisonous arsine gas. Similar hazards could also exist if high concentrations of antimony were employed in place of arsenic.

The use of antimony in place of arsenic to

activate cobalt and nickel removal with zinc dust is well known and several different processes using antimony are used commercially. Australian Patent 465,511 discloses a two stage process in which copper and cadmium are first removed at a relatively low temperature (approx. 50°C) followed by a second stage in which cobalt and nickel are precipitated in the presence of added antimony at a temperature between 80°C and the boiling point, by the addition of zinc dust preferably containing significant levels of lead. The main disadvantage of this process is the high zinc dust requirement and the need of a high second stage temperature.

Australian Patent 498,044 discloses that the second stage removal of cobalt can be improved by the deliberate addition of some copper. This has the disadvantage that the recovery of added copper from the second stage cementate is complicated. Both of the foregoing processes possess the additional disadvantage that the first stage cementate requires reprocessing to recover a high grade copper residue.

Canadian Patent 1046288 teaches that it is possible to recycle cementate between stages to reduce total zinc dust requirements. In this process copper, cadmium, and some cobalt are precipitated in a first stage in the presence of added arsenic and/or antimony using zinc dust cementates recycled from a second stage. Remaining cobalt is precipitated in the second stage in the presence of arsenic and/or antimony by the addition of fresh zinc dust

and at a high temperature. A third clean up stage is also required, the cementate from which is recycled back to the first or second stage. As a consequence of these recycles this process results in the production of only one cementate
5 containing all the removed impurities and a complex re-treatment procedure is required to recover the valuable metals copper, cadmium, and zinc from this cementate. Furthermore, the second stage cementation of cobalt still requires a temperature in excess of 90°C. Similar use of
10 preformed cementate containing As, Zn, Cu, Co, and Ni to reduce zinc dust requirements has also been described in Japanese Patent No. 55-95622. Again, all the impurities are removed in the one product and in this case the recovery of copper would require further re-processing of the
15 cementate.

DETAILED DESCRIPTION OF THE INVENTION

The applicants have found that, in the absence of copper, the presence of cadmium together with a relatively small amount of antimony has a beneficial effect
20 on
(a) the removal of cobalt with zinc dust,
(b) the stability of the resultant cementate, and
(c) the ability to leach selectively the cadmium and zinc from the cementate.

25 The present invention is based on these discoveries.

Impurity levels in the impure zinc sulphate solution to be treated will depend on the nature of the

concentrate being roasted and on the severity of the leaching conditions. Target levels of impurities will also depend on the concentration of other elements in the solution, e.g. manganese, and the particular requirements of the cellroom in question. The following ranges of impurity levels are considered typical of present and future leach liquors produced in the plant belonging to Electrolytic Zinc Company of Australasia Limited, Risdon, Tasmania, and these ranges have been used in the accompanying test examples: Cu approx. 200 mg/l, Cd 200 - 400 mg/l, Co 10 - 30 mg/l, Ni 3 - 6 mg/l. At Risdon, purification is considered satisfactory if the following impurity levels are achieved: Cu \leq 0.1 mg/l, Cd \leq 0.5 mg/l, Co 4 - 8 mg/l, Ni \leq 0.1 mg/l. In other electrolytic zinc plants Co levels of 0.1 - 0.3 mg/l are required.

In the first stage of the present process copper may be removed by cementation with zinc dust. The reaction occurs readily and although cadmium also precipitates in the early stages of the reaction it redissolves at a temperature of 65°C or above leaving a substantially pure copper precipitate. A residence time of 30 minutes or less may be employed and under mild agitation the resultant slurry is stable and may be readily thickened and filtered. As shown in Example 1, most of the cadmium, cobalt and nickel remain in solution and pass to the second stage. The composition of the copper cementate (see Example 1) is such that further processing is not required to eliminate undes-

irable impurities and the product should be readily market-
able as such. This is one feature of the present invention.
However, one skilled in the art will be aware of suitable
procedures for treating such a cementate to produce higher
5 grade products for marketing if this is required.

It will be apparent that the copper pre-
cipitated in the first stage may be separated from the copper
depleted solution or alternatively allowed to remain in a
slurry form and removed together with the cementate from
10 the second stage. This is a further feature of the present
invention.

Other means of removing copper from solution
than cementation with zinc dust may be readily employed in
the first stage, for example, cementation with metallic iron,
15 cementation with steel, precipitation as copper sulphide,
precipitation as a basic copper salt, solvent extraction and
ion exchange. This comprises an additional feature of the
present invention.

~~Furthermore, the removal of copper may not~~
20 necessarily immediately precede the second stage for cadmium,
cobalt and nickel cementation but can be separated from the
second stage by at least one other process step. This is a
further aspect of the present invention.

The decopperized solution entering the
25 second stage contains the remaining impurities cadmium,
~~cobalt and nickel. The applicants have discovered that the~~



Furthermore, the removal of copper may not necessarily immediately precede the second stage of cadmium, cobalt and nickel cementation but can be separated from the second stage by at least one other
5 process step, not necessarily connected with the present invention, for example oxidation and removal of iron from solution. This is a further aspect of the present invention.

The decopperized solution entering the second
10 stage contains the remaining impurities cadmium, cobalt and nickel. The applicants have discovered that the



presence of cadmium, in addition to antimony, results in a considerable enhancement in the rate of cobalt removal. This effect becomes greater as the cadmium level is increased up to a level of 515 mg Cd per litre, as shown in Example 2.

5 At cadmium levels of < 1 mg Cd per litre very little cobalt is removed. Between cadmium levels of 0.8 mg Cd per litre and 515 mg Cd per litre the initial pseudo first order rate constant for cobalt removal increases from $4.5 \times 10^{-3} \text{ min}^{-1}$ to $79.1 \times 10^{-3} \text{ min}^{-1}$. This is an important feature of the

10 present invention.

With cadmium present it is also possible to achieve satisfactory cobalt removal with relatively small additions of zinc dust. As shown in Example 3 a level of 1.5 g zinc dust/l gives acceptable results. However, to

15 ensure that the target cadmium level of $< 0.5 \text{ mg/l}$ is reached a level of 2 g/l is required. In Table 1 the performances of alternative patented processes are compared with the process described by the present invention.

A further feature of the present invention

20 is the ability to carry out a satisfactory cobalt purification at a temperature of less than 80°C . It is shown in Example 2 that a temperature of 75°C is adequate at a zinc dust addition of 2 g per litre and an antimony addition of 1 mg per litre providing that 100 mg per litre

25 or more of cadmium is initially present. Cadmium removal is also satisfactory.

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By lowering the temperature of the pulp to less than 65°C at a later point within the second stage, but preceding the solid-liquid separation step, it is possible to achieve even lower cadmium levels of ≤ 0.2 mg/l.

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It has also been found that the separate addition of a further 0.5 g/l or less of zinc dust together with a small amount of spent electrolyte to a later point within the second stage also may have a beneficial effect in lowering the final cadmium level. The ability to operate the second

stage at a temperature of 75°C is particularly advantageous in that the solution does not have to be heated between the first and second stages. Thus the need for expensive heat exchangers is diminished.

5 Australian Patent 498,044 describes a process in which additional copper is added to improve the efficiency of cobalt precipitation. A series of tests was performed to assess the effect of additions of soluble copper on the degree of cobalt removal in the presence of
10 cadmium, with results as shown in Example 4. It is shown conclusively that there is no significant advantage to be obtained by adding copper and, in fact, that levels of copper in excess of 26 mg per litre tend to cause serious cadmium reversion.

15 The effect of varying the temperature between 65°C and 85°C is shown in Example 5.

 The applicants have also discovered that the absence of copper in the cementate resulting from the second stage purification process facilitates the recovery
20 of zinc and cadmium when the cementate is leached in spent electrolyte and also improves the selectivity of zinc and cadmium dissolution over cobalt and nickel (see Example 6). This is an additional important feature of the present invention.

25 Although cadmium exerts a significant influence on the rate of cobalt removal, antimony is still

required. However, an antimony level of 0.5 - 1.0 mg per litre only is adequate and, in fact, higher levels have no significant effect on the rate of cobalt removal and tend to cause increased reversion of cadmium, as shown in

5 Example 7. Thus, the need for excessive quantities of activating agent such as antimony or arsenic is circumvented. This gives the present invention a distinct advantage over the process described in Australian Patent 499,355 in which sufficient arsenic trioxide must be added to give an
10 arsenic to cobalt ratio (gram per gram) in solution of at least 3. This is another advantageous feature of the present invention which typically requires only an antimony to cobalt ratio of 0.05.

The lead level in the zinc dust has an
15 appreciable effect on the rate of cobalt removal in the presence of cadmium, as shown by Example 8. Thus, although cadmium in solution exerts an activating effect in the absence of lead, its effect is much more marked when lead is present. This comprises a further aspect of the present
20 invention.

It has also been discovered by the applicants that the addition of a relatively small amount of cadmium to the zinc dust helps to limit the degree of cadmium reversion. Thus, the addition of both cadmium and
25 lead to the zinc dust prior to cementation will yield additional significant benefits in producing the maximum

degree of cobalt and cadmium removal. This feature comprises an additional aspect of the present invention.

Furthermore, if elemental sulphur is added in addition to antimony, a significant improvement in the rate of cobalt precipitation can be achieved, as shown in Example 9. This is an additional feature of the present invention.

Example 10 describes the use of recycled solids to precipitate cobalt and cadmium in a simulated
10 counter-current operation entirely within the second stage of zinc dust purification, that is, within the stage for cadmium, cobalt and nickel removal. The results indicate that the recycled solids may be used to significantly lower solution impurity levels, thus allowing even lower overall
15 zinc dust usage levels.

It will readily be appreciated by one skilled in the art that both the first and second stages may be operated in a counter-current manner with solids recycled within either stage, but not between stages, if
20 desired.

The superiority of the new process described in the present invention over the other purification processes described herein has been demonstrated experimentally and the results of these tests are shown in Example 11.

25 The process disclosed in Australian Patent 465,511 utilizes a two stage procedure in which cobalt is

removed from a solution free of both copper and cadmium.
Despite the use of twice the quantity of zinc dust compared
with the process of the present invention the rate of cobalt
removal is significantly worse. The process disclosed in

- 5 Australian Patent 498,044 makes use of a small copper
addition (20 mg/l) to improve the rate of cobalt precipita-
tion and reduce the zinc dust requirement. However, the
results are still measurably inferior to those obtained by
the process of the present invention (Example 11 (b)).
- 10 Where recycled cementate is employed to remove cobalt from
solution still containing both copper and cadmium, as
described in Canadian Patent 1046288, the rate of cobalt
removal is increased but only at the expense of a higher
zinc dust addition amounting to twice the requirement of
- 15 the process of the present invention (see Example 11 (c)).
Finally, where large quantities of antimony are employed
and the resulting metal-antimonide compounds are repeatedly
contacted with fresh copper-free impure solution, as
described in Australian Patent 499,355, no appreciable
- 20 reduction in zinc dust requirements can be achieved
(Example 11 (d)). In fact, the results suggest that this
method of operation would result in an actual decrease in
the rate of cobalt precipitation compared to that achievable
using the process of the present invention. In addition,
- 25 cadmium neither fully reverts nor is completely precipitated.

The relative performances of each of the

above mentioned processes are summarized in Table 1. It is evident that the process described of the present invention is capable of achieving the highest rate as well as the greatest degree of cobalt precipitation simultaneously with a relatively low consumption of zinc dust.

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TABLE 1

Comparison of Alternative Purification Processes for removal of Cobalt

Patent No.	Activator	Zinc dust requirement (g/l)	Temperature (°C)	$10^2 \times k_{Co}^*$ (min ⁻¹)	Cobalt precipitated in two hours (%)
Aust. 465,511	Sb	4.0	75	0.47	37.0
Aust. 498,044	Sb + Cu	2.0	75	1.86	86.2
Can. 1046288	Sb	4.0 (recycled cementate)	75	4.60	95.5
Aust. 499,355	Metal antimonide	2.0	75	approx. 1.5	< 42.7
Process of the present invention	Sb + Cd Cd = 515 mg/l	2.0	75	7.91	99.4

* Initial pseudo first order rate constant for cobalt removal.

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TABLE 1

Comparison of Alternative Purification Processes for removal of Cobalt

Patent No.	Activator	Zinc dust requirement (g/l)	Temperature (°C)	$10^2 \times k_{Co}^*$ (min ⁻¹)	Cobalt precipitated in two hours (%)
Aust. 465,511	Sb	4.0	75	0.47	37.0
Aust. 498,044	Sb + Cu	2.0	75	1.86	86.2
Can. 1046288	Sb	4.0 (recycled cementate)	75	4.60	95.5
Aust. 499,355	Metal antimonide	2.0	75	approx. 1.5	< 42.7
Process of the present invention	Sb + Cd Cd = 515 mg/l	2.0	75	7.91	99.4

* Initial pseudo first order rate constant for cobalt removal.

The process of the present invention is illustrated by the following non-limiting examples.

Example 1 - First stage removal of copper

The required quantity of zinc dust (-60
5 mesh Tyler) was added to the impure solution (4 l) in a
baffled 5 l beaker at 80 - 85°C and the suspension was
agitated with a 6-bladed turbine impeller rotating at
250 rpm at this temperature for 60 minutes. The quantity
of zinc dust was varied according to the stoichiometric
10 level required, based on the requirement for precipitation
of copper according to the reaction $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}^0$.

The variation of solution composition with
time is shown below:

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Zinc dust (% stoichio- metric)	170		120		95		75	
Temp. (°C)	80		85		85		85	
Test No.	A		B		C		D	
	Solution Composition (mg/l)		Solution Composition (mg/l)		Solution Composition (mg/l)		Solution Composition (mg/l)	
Time (min)	Cu	Cd	Cu	Cd	Cu	Cd	Cu	Cd
0	225	250	195	245	210	240	215	260
5	33.5		80	160	170	193	115	235
10	7.5		32	200	46	220	71	230
20	0.3		10	220	48	233	90	225
40	< 0.2		1	245	61	230	94	250
60	< 0.2	190	< 1	245	60	250	107	255
120					81	245	138	260

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Zinc dust (% stoichio- metric)	170		120		95		75	
Temp. (°C)	80		85		85		85	
Test No.	A		B		C		D	
	Solution Composition (mg/l)		Solution Composition (mg/l)		Solution Composition (mg/l)		Solution Composition (mg/l)	
Time (min)	Cu	Cd	Cu	Cd	Cu	Cd	Cu	Cd
0	225	250	195	245	210	240	215	260
5	33.5		80	160	170	193	115	235
10	7.5		32	200	46	220	71	230
20	0.3		10	220	48	233	90	225
40	< 0.2		1	245	61	230	94	250
60	< 0.2	190	< 1	245	60	250	107	255
120					81	245	138	260

Solutions used for all tests were obtained from the Risdon zinc plant circuit and contained typical levels of Zn 100 g/l, Mn 10 g/l, Co 25 - 30 mg/l, Ni 2 - 5 mg/l, As 0.1 mg/l, Sb \leq 0.1 mg/l. Cobalt and nickel levels for Run B were monitored and no significant change in concentration was observed for these elements. The formation of Cu_2Cd during the first 10 - 20 minutes of Run B was confirmed by XRD analysis. The initial pH_{25° of all solutions was 4.5 - 5.5 and was not adjusted during the reaction. The tests, above, with the exception of Test A were carried out using zinc dust containing 0.8% Pb. However, it is possible to achieve very similar results using non-leaded dust.

If the degree of agitation is increased it is also possible to operate at a lower temperature but still maintain the desired reversion of cadmium as shown by the following test:

Zinc dust (% stoichiometric)	120	
Temperature (°C)	65	
Agitation rate (r.p.m.)	600	
Time (min)	Solution composition (mg/l)	
	Cu	Cd
0	205	245
5	80	195
10	18	213
20	2	220
40	7	230
60	37	240
120	135	250

Unfortunately, copper also tends to revert under these conditions. The physical form of the cementate also changed : in this test the final cementate was fine and light-brown in colour, while in Test B (85°C, 250 rpm) the final cementate consisted of red-brown coloured flocs.

The composition of the cementate obtained using conditions as described for Run B above, is shown below:

	%
Cu	92.1
Cd	1.2
Zn	1.4
H ₂ O	1.3

In the following examples, Nos. 2 - 5, the second stage removal of cobalt, cadmium and nickel is illustrated and in Example No. 6 one procedure for the treatment of the second stage cementate for zinc and cadmium recovery is described. The following general procedure was employed for the cementation tests:

Zinc dust (-60 mesh Tyler) was added to pre-heated de-copperized impure solution (4 l) in a 5 l baffled beaker at an initial pH_{25° of 4.0 and agitated at this temperature for 2 to 4 hours.

Agitation was supplied by a 6-bladed turbine impeller, (7.5 cm in diameter) rotating at 300 rpm. Where necessary, the levels of cadmium, copper, and antimony in the initial solution were adjusted by addition of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6 \cdot 1/2\text{H}_2\text{O}$, respectively. During each test samples were withdrawn from the beaker at selected times through a sintered glass filter and analyzed. Solutions used in all tests were obtained from the Risdon zinc plant circuit and contained typical background levels of 100 g Zn/l, 10 g Mn/l, 0.1 mg As/l, < 0.1 mg Sb/l, and < 0.1 mg Fe/l.

In some of the examples which follow the rate of cobalt removal is expressed by the initial pseudo first-order rate constant, k_{Co} .

Example 2 - Effect of Initial Cadmium Concentration on Rate of Cobalt Removal

Zn dust 2 g/l, Sb 1 mg/l, 75°C

		Co (mg/l)						
Initial Cadmium concentration (mg/l)		0.8	12	48	100	160	335	515
Time (min)	0	18.8	18.2	18.2	18.8	18.4	16.4	16.8
	10	18.8	17.8	16.4	16.8	15.0	13.2	11.6
	30	16.8	15.8	15.0	12.9	10.6	6.8	0.6
	60	14.6	14.0	12.6	9.2	5.6	1.8	1.8
	90	14.2	12.8	10.2	6.4	3.4	1.2	0.2
	120	13.6	11.8	11.0	4.3	2.4	0.3	0.1
$10^2 \times k_{Co} \text{ (min}^{-1}\text{)}$		0.45	0.46	0.62	1.22	1.89	3.29	7.91

This example demonstrates the significant effect that cadmium has on the rate of cobalt removal.

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Example 2 - Effect of Initial Cadmium Concentration on Rate of Cobalt Removal

Zn dust 2 g/l, Sb 1 mg/l, 75°C

		Co (mg/l)						
Initial Cadmium concentration (mg/l)		0.8	12	48	100	160	335	515
Time (min)	0	18.8	18.2	18.2	18.8	18.4	16.4	16.8
	10	18.8	17.8	16.4	16.8	15.0	13.2	11.6
	30	16.8	15.8	15.0	12.9	10.6	6.8	0.6
	60	14.6	14.0	12.6	9.2	5.6	1.8	1.8
	90	14.2	12.8	10.2	6.4	3.4	1.2	0.2
	120	13.6	11.8	11.0	4.3	2.4	0.3	0.1
$10^2 \times k_{CO} \text{ (min}^{-1}\text{)}$		0.45	0.46	0.62	1.22	1.89	3.29	7.91

This example demonstrates the significant effect that cadmium has on the rate of cobalt removal.

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Zn dust addition (g/l)	1.5			2.0			4.0		
Time (min)	Co	Cd	Ni	Co	Cd	Ni	Co	Cd	Ni
0	16.5	390	3.8	19.0	405	3.8	18.0	410	3.8
10	12.0	39	-	13.8	25	2.4	13.0	6.3	-
30	5.8	0.85	-	6.6	0.25	0.55	3.8	1.0	-
60	1.5	-	-	2.2	0.35	0.1	0.3	-	-
90	-	-	-	0.9	0.45	0.1	-	-	-
120	0.1	0.7	-	-	-	-	<0.1	.55	-
180	< 0.1	0.75	-	0.5	0.80	0.1	0.2	.55	-
240	0.14	2.4	0.1	-	-	-	0.02	.70	.25
$10^2 \times k_{Co} \text{ (min}^{-1}\text{)}$	4.0			3.6			6.9		

This example shows that a zinc dust addition of 1.5 g/l will give satisfactory purification for cobalt but that a level of 2.0 g/l is necessary to achieve the target

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Example 3 - Effect of Zinc Dust additions

(Sb 1 mg/l, 75°C)

Zn dust addition (g/l)	1.5			2.0			4.0		
Time (min)	Co	Cd	Ni	Co	Cd	Ni	Co	Cd	Ni
0	16.5	390	3.8	19.0	405	3.8	18.0	410	3.8
10	12.0	39	-	13.8	25	2.4	13.0	6.3	-
30	5.8	0.85	-	6.6	0.25	0.55	3.8	1.0	-
60	1.5	-	-	2.2	0.35	0.1	0.3	-	-
90	-	-	-	0.9	0.45	<0.1	-	-	-
120	0.1	0.7	-	-	-	-	<0.1	.55	-
180	< 0.1	0.75	-	0.5	0.80	<0.1	0.2	.55	-
240	0.14	2.4	0.1	-	-	-	0.02	.70	.25
$10^2 \times k_{Co} \text{ (min}^{-1}\text{)}$	4.0			3.6			6.9		

This example shows that a zinc dust addition of 1.5 g/l will give satisfactory purification for cobalt but that a level of 2.0 g/l is necessary to achieve the target

cadmium level of ≤ 0.5 mg/l at this particular temperature (75°C) and antimony level (1 mg/l). With a final nickel concentration of ≤ 0.1 mg/l, nickel removal is considered acceptable at either zinc dust addition rate.

Example 4 - Effect of Copper on the Rate of Cobalt Removal

(Zn dust 2 g/l, Sb 1 mg/l, 75°C)

Initial Cu (mg/l)	0		2.2		10		26		44		95	
Time (min)	Co	Cd	Co	Cd	Co	Cd	Co	Cd	Co	Cd	Co	Cd
0	11.7	395	12.4	390	12	390	12	400	12.6	385	12	380
10	8.5	23	8.6	20	8.8	26	8.0	8	8.3	2.8	4.0	2.2
30	3.0	0.45	2.8	0.1	2.8	1.0	2.1	0.2	1.9	0.2	3.0	0.1
60	0.8	-	0.4	0.15	0.4	0.5	0.2	0.15	0.3	0.2	2.8	0.65
90	0.4	-	0.1	0.75	<0.1	0.1	<0.1	0.5	0.2	0.7	2.2	1.6
180	0.07	0.65	<0.1	0.4	<0.1	0.25	<0.1	0.7	0.3	4.8	1.8	8.7

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cadmium level of ≤ 0.5 mg/l at this particular temperature (75°C) and antimony level (1 mg/l). With a final nickel concentration of ≤ 0.1 mg/l, nickel removal is considered acceptable at either zinc dust addition rate.

Example 4 - Effect of Copper on the Rate of Cobalt Removal

(Zn dust 2 g/l, Sb 1 mg/l, 75°C)

Initial Cu (mg/l)	0		2.2		10		26		44		95	
Time (min)	Co	Cd	Co	Cd	Co	Cd	Co	Cd	Co	Cd	Co	Cd
0	11.7	395	12.4	390	12	390	12	400	12.6	385	12	380
10	8.5	23	8.6	20	8.8	26	8.0	8	8.3	2.8	4.0	2.2
30	3.0	0.45	2.8	0.1	2.8	1.0	2.1	0.2	1.9	0.2	3.0	0.1
60	0.8	-	0.4	0.15	0.4	0.5	0.2	0.15	0.3	0.2	2.8	0.65
90	0.4	-	0.1	0.75	<0.1	0.1	<0.1	0.5	0.2	0.7	2.2	1.6
180	0.07	0.65	<0.1	0.4	<0.1	0.25	<0.1	0.7	0.3	4.8	1.8	8.7

These tests indicate that there is very little benefit in the rate of cobalt removal to be obtained by adding soluble copper to the solution. There is some evidence that slightly lower final cadmium levels might be achieved at copper levels of 10 mg/l or less but at copper levels of between 26 and 95 mg/l the reversion of cadmium in the later stages of the reaction becomes pronounced.

Example 5 - Effect of Temperature on Cobalt Removal

(Zn dust 2 g/l, Sb 1 mg/l, Cd 250 mg/l)

	Solution Composition (mg/l)		
Temperature (°C)	65	75	85
Time (min)	Co	Co	Co
0	26.5	25.0	24.8
10	24.3	21.5	17.0
30	21.3	15.2	7.1
60	19.3	10.5	2.3
90	18.6	7.5	1.3
120	18.4	8.0	1.1

This example shows that satisfactory removal of cobalt may be achieved at a temperature of as low as 75°C.

Example 6 - Recovery of Zinc and Cadmium from the
second stage cementate

(a) Copper-free cementate

Spent electrolyte containing 110 g H_2SO_4 /l was metered
5 under pH control into 4 litres of a mildly-agitated slurry
containing 40 g of second stage cementate at ambient temp-
erature to maintain a pH_{25° of > 4.0 . The cementate con-
tained 73.5% Zn, 20.0% Cd, 1.7% Co and 0.29% Ni. The re-
action virtually ceased after 48 hours and the residue
10 (0.91 g solids/l) was recovered by filtration, washed, and
dried under vacuum. Composition of the residue was 14.1%
Zn, 16.4% Co, 23.0% Cd and 2.8% Ni. Calculated extractions
were 98.3% Zn, 89.5% Cd, 12.2% Co and 12.1% Ni.

(b) Cementate containing copper

15 A cementate of composition 52.9% Zn, 8.4% Cd, 0.79% Co,
0.16% Ni and 2.0% Cu was produced by conducting a normal
second stage purification on solution to which had been
added additional soluble copper. After leaching 40 g of
this cementate as described under (a) above, a final residue
20 (4.3 g) was obtained containing 6.2% Zn, 24.6% Cd, 5.2% Co,
1.2% Ni and 16% Cu. Calculated extractions were 96.7% Zn,
68.5% Cd, 29.2% Co and 19.4% Ni.

This example demonstrates that the presence of copper in
the cementate seriously impedes the selective dissolution
25 of zinc and cadmium.

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Example 7 - Effect of Sb on the rate of Cobalt Removal

(Zn dust 2 g/l, 75°C)

	Solution Composition (mg/l)											
Sb level (Mg/l)	0.75			4.0			7.4			95		
Time (min)	Co	Cd	Sb	Co	Cd	Sb	Co	Cd	Sb	Co	Cd	Sb
0	15.0	320		18	320		19.6	335		17	325	
10	13.9	28		16.8	8.7		18.0	18		16.2	2.8	
30	6.5	0.5		10	0.75		11.6	1.3		8.6	5.8	
60	2.1	-		6.6	1.0		7.8	1.6		6.6	10	
90	0.7	-		5.0	2.2		6.2	2.6		5.4	8.6	
180	0.05	0.6	<0.01	4.0	3.0	.04	4.6	4.0	.19	3.8	14	0.9
$10^2 \times k_{Co} (\text{min}^{-1})$	3.27			1.76			1.60			1.70		

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Example 7 - Effect of Sb on the rate of Cobalt Removal

(Zn dust 2 g/l, 75°C)

Sb level (Mg/l)	Solution Composition (mg/l)											
	0.75			4.0			7.4			95		
Time (min)	Co	Cd	Sb	Co	Cd	Sb	Co	Cd	Sb	Co	Cd	Sb
0	15.0	320		18	320		19.6	335		17	325	
10	13.9	28		16.8	8.7		18.0	18		16.2	2.8	
30	6.5	0.5		10	0.75		11.6	1.3		8.6	5.8	
60	2.1	-		6.6	1.0		7.8	1.6		6.5	10	
90	0.7	-		5.0	2.2		6.2	2.6		5.4	8.6	
180	0.05	0.6	<0.01	4.0	3.0	.04	4.6	4.0	.19	3.8	14	0.9
$10^2 \times k_{Co} (\text{min}^{-1})$	3.27			1.76			1.60			1.70		

This example illustrates the relative insensitivity of the rate of cobalt removal to antimony additions of between 0.75 mg/l and 95 mg/l. At levels of between 4 mg/l and 95 mg/l, however, there is an increase
5 in the rate of cadmium reversion and the level of antimony in the solution after a 3 hour purification also becomes unacceptably high at the maximum addition rate tested.

Example 8 - Composition of Zinc Dust

Four zinc dusts containing different levels
10 of Pb were tested. In addition, the effect of enriching the dust with Cd was also determined. The results are shown in the following tables:

Zinc dust, 2 g/l, Sb 1 mg/l, 75°C

Zinc dust* type	A		B		C		D	
Time (min)			Solution Composition Mg/l)					
	Co	Cd	Co	Cd	Co	Cd	Co	Cd
0	20	380	18	380	18	380	19	380
10	14.4	18	12.5	18	12.5	12	13.2	18
30	7.3	1.2	3.5	1.2	5.4	1	8.5	< 1
60	6.8	1.2	1.9	2.1	2.0	1	6.6	< 1
90	6.4	1.5	1.6	3.2	1.4	1.2	5.9	< 1
120	6.1	2.5	< 1	3.2	< 1	0.4	5.3	< 1
180	7.0	4.3	0.2	4.3	< 0.1	0.9	4.7	1.3

*Zinc dust composition : A Pb < 0.01%, Cd < 0.01%

B Pb 0.12%, Cd 0.0095%

C Pb 0.8%, Cd 0.0013%

D Pb 0.01%, Cd 0.6%

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Zinc dust, 2 g/l, Sb 1 mg/l, 75°C

Zinc dust* type	A		B		C		D	
Time (min)			Solution Composition Mg/l)					
	Co	Cd	Co	Cd	Co	Cd	Co	Cd
0	20	380	18	380	18	380	19	380
10	14.4	18	12.5	18	12.5	12	13.2	18
30	7.3	1.2	3.5	1.2	5.4	1	8.5	< 1
60	6.8	1.2	1.9	2.1	2.0	1	6.6	< 1
90	6.4	1.5	1.6	3.2	1.4	1.2	5.9	< 1
120	5.1	2.5	< 1	3.2	< 1	0.4	5.3	< 1
180	7.0	4.3	0.2	4.3	< 0.1	0.9	4.7	1.3

*Zinc dust composition : A Pb < 0.01%, Cd < 0.01%

B Pb 0.12%, Cd 0.0095%

C Pb 0.8%, Cd 0.0013%

D Pb 0.01%, Cd 0.6%

It is evident from these results that the addition of lead to the zinc dust has a marked improvement on the final cobalt level achieved after 3 hour reaction although the rate of cobalt removal, measured during the early part of tests, does not vary appreciably. Cadmium reversion was also less pronounced at the highest Pb level (Zinc dust C). The addition of Cd to the dust (Zinc dust D, 0.6% Cd) did not result in any appreciable improvement in cobalt removal but helps to limit the degree of cadmium reversion, when compared with the Cd- and Pb-free dust (A).

Particle size distributions for each zinc dust are also shown below:

Cumulative weight undersize (%)				
Sieve size (μ m)	A	B	C	D
300	96.7	96.0	97.4	96.9
150	77.4	74.1	85.0	79.2
75	52.8	50.1	58.1	57.2
45	31.2	31.2	32.4	35.8
38	23.7	25.6	21.2	28.0
Mean particle size (μ m)	72	78	66	66

It is evident that there is only a minor variation in particle size and therefore the variations observed in reactivity are primarily due to changes in composition of the zinc dusts.

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Example 9 - Use of Elemental Sulphur in addition to Antimony

(Zinc dust, 2 g/l, 75°C)

Elemental Sulphur addition (mg/l)	0				500			
Time (min)	Solution Composition (mg/l)				Solution Composition (mg/l)			
	Co	Cd	Ni	Sb	Co	Cd	Ni	Sb
0	25.0	245	3.8	1.0	26.5	260	4.9	0.96
10	21.5	18			22.9	14		
30	15.2	1			14.1	0.3		
60	10.5	1			7.1	0.6		
90	7.5	1.2			3.4	0.45		
120	8.0	1.4	<0.1	-	2.1	1.0	0.1	0.02
$10^2 \times k_{Co} \text{ (min}^{-1}\text{)}$	1.46				2.38			

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Example 9 - Use of Elemental Sulphur in addition to Antimony

(Zinc dust, 2 g/l, 75°C)

Elemental Sulphur addition (mg/l)	0				500			
Time (min)	Solution Composition (mg/l)				Solution Composition (mg/l)			
	Co	Cd	Ni	Sb	Co	Cd	Ni	Sb
0	25.0	245	3.8	1.0	26.5	260	4.9	0.96
10	21.5	18			22.9	14		
30	15.2	1			14.1	0.3		
60	10.5	1			7.1	0.6		
90	7.5	1.2			3.4	0.45		
120	8.0	1.4	<0.1	-	2.1	1.0	0.1	0.02
$10^2 \times k_{CO} \text{ (min}^{-1}\text{)}$	1.46				2.38			

Example 10 - Use of Recycled solids

This example describes the batchwise simulation of a stage 2 counter-current recycle operation. Fresh solution derived from stage 1 was treated with a small amount (1.5 g/l) of zinc dust, the solids removed and the filtrate treated with 2 g/l zinc dust for 60 minutes at 80°C. After this time the solids were settled and the supernatant decanted. Fresh solution derived from stage 1 (80°C) was then added to these solids together with 1 mg Sb/l and the operating conditions maintained as before. The solution concentrations were monitored with time, as shown below.

Time (mins)	Solution Composition (mg/l)	
	Co	Cd
0	24.1	415
10	18.3	23
30	15.0	0.8
60	13.0	1.5
90	12.2	3.6
120	12.1	6.7
180	11.9	35

This example shows that recycled solids are effective in precipitating cobalt and especially cadmium. However some reversion of the cadmium may occur if long residence times are employed. Thus some benefit in terms of lower zinc dust usage may be achieved by incorporating a counter-current recycle of cementate within the second stage.

Example 11

(a) Treatment according to the process described in Austrian Patent 465,511.

Zinc dust (-60#, 0.8% Pb), 4 g/l

Sb 1 mg/l, No Cu, No Cd

Temperature (°C)	75	85	95
Time (min)	Co	Co	Co
5	27.4	22.8 (24.8)*	26.6
10	25.8	21.6 (17.0)	20.8
30	23.4	14.4 (7.1)	11.2
60	20.6	10.7 (2.3)	5.6
90	18.4	7.9 (1.3)	2.8
120	17.3	6.2 (1.1)	1.8
$10^2 \times k_{Cc} \text{ (min}^{-1}\text{)}$	0.47	1.35 (3.99)	2.63

*bracketed values obtained (zinc dust, 2 g/l, Sb 1 mg/l, Cd 240 mg/l) using the process of the present invention.

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Example 11

(a) Treatment according to the process described in Australian Patent 465,511.

Zinc dust (-60#, 0.8% Pb), 4 g/l

Sb 1 mg/l, No Cu, No Cd

Temperature (°C)	75	85	95
Time (min)	Co	Co	Co
0	27.4	22.8 (24.8)*	26.6
10	25.8	21.6 (17.0)	20.8
30	23.4	14.4 (7.1)	11.2
60	20.6	10.7 (2.3)	5.6
90	18.4	7.9 (1.3)	2.8
120	17.3	6.2 (1.1)	1.8
$10^2 \times k_{Co} \text{ (min}^{-1}\text{)}$	0.47	1.35 (3.99)	2.63

*bracketed values obtained (zinc dust, 2 g/l, Sb 1 mg/l, Cd 240 mg/l) using the process of the present invention.

These results show that significantly improved results are obtained using the process of the present invention in spite of halving the zinc dust addition. This improvement is a function of the activating effect of cadmium described previously.

(b) Treatment according to the process described in Australian Patent 498,044.

Process	According to Australian Patent 498,044	According to the process of the present invention
Operating Conditions	Zinc dust (-250#, 0.8% Pb), 2 g/l; Sb 1 mg/l; Cu 20 mg/l; No Cd; 75°C	Zinc dust (-60#, 0.8% Pb), 2 g/l; Sb 1 mg/l; Cd 380 mg/l; No Cu; 75°C
Time (min)	Solution Composition Co (mg/l)	Solution Composition Co (mg/l)
0	21.8	18.0
10	16.8	12.5
30	9.5	5.4
60	6.0	2.0
120	3.0	< 1.0
180	1.8	< 0.1
$10^2 \times k_{Co} \text{ (min}^{-1}\text{)}$	1.86	3.7

Again results obtained using the process of the present invention are considerably better than those obtained following examples in Australian Patent 498,044 where Cu (20 mg/l) is added to activate cobalt removal from cadmium-free solutions.

5 (c) Treatment according to the process described in Canadian Patent 1,046,288.

This process is operated in two or three stages with recycle of cementate between stages to produce a single zinc dust cementate containing all the impurity metals. A laboratory batch simulation gave the following results:

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Stage*	Zinc d st (g/l)	Antimony (mg/l)	Temp. (°C)	Time (min)	Solution composition (mg/l)			
					Co	Cu	Cd	Ni
I	Recycled cementate	1.0	85	0	30	255	280	2.5
				10	28.4	1.0	1.7	1.1
				30	13.4	0.13	0.4	<1.0
				60	12.8		160	
				90	14.5		250	
				120	17.0		295	
				150	22.0	0.03	355	0.1
II	4.0	0.5	75	0	22.0	0.03	355	0.1
				5	15.5		24	
				15	11.7		0.6	
				30	6.2		0.7	
				60	1.3		0.75	
				120	1.0		1.0	

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Stage*	Zinc dust (g/l)	Antimony (mg/l)	Temp. (°C)	Time (min)	Solution composition (mg/l)			
					Co	Cu	Cd	Ni
I	Recycled cementate	1.0	85	0	30	255	280	2.5
				10	28.4	1.0	1.7	1.1
				30	13.4	0.13	0.4	<1.0
				60	12.8		160	
				90	14.5		250	
				120	17.0		295	
				150	22.0	0.03	355	0.1
II	4.0	0.5	75	0	22.0	0.03	355	0.1
				5	15.5		24	
				15	11.7		0.6	
				30	6.2		0.7	
				60	1.3		0.75	
				120	1.0		1.0	

* The cementate used in Stage I was made by treating a solution of similar composition to that used in Stage II with 4 g/l of zinc dust (-60#, 0.8% Pb) and 0.5 mg/l of antimony at 75°C for 2 hours. In Stage II, fresh zinc
5 dust was reacted with the solution from Stage I from which the solids had been removed by decantation of the supernatant liquor after settling.

The above results indicate that solution purification is achieved fairly efficiently using this two
10 stage procedure, but that twice the amount of zinc dust is required compared to the process of the present invention and reversion of two of the precipitated metals is pronounced in Stage I. In addition, recovery of metals from the cementate which has been produced using the procedure
15 described in Canadian Patent 1046288 would be expected to be more difficult, as shown by Example 6.

(d) Treatment according to the process described in Australian Patent 499,355.

In this process a large quantity of
20 activating agent such as arsenic or antimony is added with the zinc dust to enable metal arsenides or antimonides to form. These compounds are then recycled and used to activate or precipitate further cobalt and nickel. Copper-free solution may be used.

25 Using antimony as the activator in sufficient quantity to theoretically form the compounds MSb (M = Co, Ni), the process was carried out batchwise in

the following manner:

Zinc dust (2 g/l, -60#, 0.8% Pb), and potassium antimonyl tartrate (145 mg/l, equivalent to 55 mg Sb/l) were added to copper-free impure solution heated to 75°C and agitated at 350 rpm. After 1 hour reaction the solids were allowed to settle, the supernatant liquor decanted and 4 l of fresh impure solution added to the same reaction vessel. The same quantities of antimony and zinc dust were then added and the reaction repeated. This procedure was carried out a further four times and the solution analysed at the conclusion of each cycle. The following results were obtained:

Cycle No.	Zinc dust addition (g/l)	Solution composition at end of cycle (mg/l)			
		Co	Cd	Ni	Sb
0	0	22.0	255	4.8	50 (initial solution)
1	2	12.6	12.0	0.9	0.04
2	2	12.6	9.0	0.65	0.06
3	2	13.4	10.0	0.5	0.36
4	1	14.7	7.4	0.45	0.14
5	1	15.5	12.0	0.60	0.24
6	0.5	16.7	9.0	0.60	0.20

The above results suggest that antimony is an unsuitable replacement for arsenic in the examples quoted in Australian Patent 499,355. Examples 2 - 5 as detailed

above show that the process of the present invention yields superior removal of both cobalt and cadmium and requires considerably smaller additions of activating agent.

It will be clearly understood that the invention in its general aspects is not limited to the specific details referred to hereinabove.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of purifying zinc sulphate solutions from an electrolytic zinc plant to precipitate the impurities copper, cadmium, cobalt and nickel by a two-stage procedure consisting of the following stages:

Stage 1: Treatment of the said solution to precipitate copper using at least one procedure drawn from the group consisting of cementation with zinc dust, cementation with metallic iron, cementation with steel, precipitation as a copper sulphide, precipitation as a basic salt, solvent extraction and ion exchange.

Stage 2: Addition of zinc dust to the copper depleted solution in the range 1 to 6 grams of zinc dust per litre of solution, in the presence of cadmium and added antimony to precipitate cadmium, cobalt and nickel from the said solution at a temperature from 65°C to the boiling point of the solution at atmospheric pressure, the resultant cementate being then separated from the then purified solution.

2. A method according to Claim 1 in which an amount of zinc dust within the range 75% to 150% of the stoichiometric requirement to precipitate copper in the zinc sulphate solution is added in the first stage at a temperature in the range 65°C to the boiling point of the solution at atmospheric pressure.

3. A method according to Claim 1 or Claim 2 in which the cementate from the first stage is separated from the copper depleted solution.

10 4. A method according to any one of Claims 1 to 3 in which the said stage 1 for precipitating copper is separated from said stage 2 for cementation of cadmium, cobalt and nickel by at least one other process step and thus does not immediately precede the aforesaid
15 stage 2.



~~2. A method according to Claim 1 in which~~

an amount of zinc dust within the range 75% to 150% of the stoichiometric requirement to precipitate copper in the zinc sulphate solution is added in the first stage at a temperature in the range 65°C to the boiling point of the solution at atmospheric pressure.

3. A method according to Claim 1 or Claim 2 in which the cementate from the first stage is separated from the copper depleted solution.

4. A method according to any one of Claims 1 to 3 in which the first stage copper precipitation is undertaken more than one stage ahead of and removed from the second stage for cadmium, cobalt and nickel cementation and thus does not immediately precede the aforesaid second stage.

5. A method according to any one of Claims 1 to 4 in which the temperature of the first stage is maintained between 75 and 95°C.

6. A method according to any one of Claims 1 to 5 in which the temperature of the second stage is maintained between 70 and 90°C.

7. A method according to any one of Claims 1 to 6 in which the temperature of the pulp within the second stage is lowered from between 70 and 90°C to less than 65°C before the subsequent solid liquid separation step.



8. A method according to any one of Claims 1 to 7 in which the amount of zinc dust added to the impure solution in stage 1 is varied between 110 and 130% of the stoichiometric requirement to precipitate the copper in the said solution.

9. A method according to any one of Claims 1 to 8 in which the antimony added to the second stage is drawn from the group containing water soluble antimony compounds, Sb_2O_3 , Sb_2S_3 , antimony metal, and antimony alloyed with the zinc dust.

10. A method according to any one of Claims 1 to 9 in which the antimony is added in a quantity between 0.5 and 10 mg antimony per litre of zinc sulphate solution.

11. A method according to any one of Claims 1 to 10 in which in the second stage the lead is present primarily as an alloy with the zinc dust used, the lead content of the zinc dust being in the range 0.1% to 2.0%.

12. A method according to any one of Claims 1 to 11 in which in the second stage the lead is added as a lead salt to the zinc sulphate solution entering stage 2, the quantity of lead salt added being equivalent to 20 to 100 mg of lead per litre of solution.

13. A method according to any one of Claims 1 to 12 in which zinc dust is added to the second stage at two separate points.

14. A method according to any one of Claims 1 to 13 in which elemental sulphur is added to the second stage in a quantity of from 100 mg to 5 g of elemental sulphur per litre of zinc sulphate solution.

15. A method according to any one of Claims 1 to 14 in which additional cadmium is added to the solution within the second stage, the said cadmium being drawn from the group containing water-soluble cadmium compounds, zinc sulphate solutions containing cadmium, cadmium metal, cadmium alloyed with zinc dust.

16. A method according to any one of Claims 1 to 15 in which the quantity of cadmium added is less than 5g per litre of zinc sulphate solution.

17. A method according to any one of Claims 1 to 16 in which spent electrolyte is added to the second stage.

18. A method according to any one of Claims 1 to 17 in which at least one of the cementation reactions is carried out in a batchwise fashion.

19. A method according to any one of Claims 1 to 18 in which at least one of the cementation reactions is carried out in a continuous fashion.

20. A method according to any one of Claims 1 to 19 in which at least one of the cementation reactions is carried out in a counter-current manner.

21. A method of purifying zinc sulphate solutions according to any one of Claims 1 to 20 and substantially as hereinbefore described with reference to the Examples.

DATED THIS 18th DAY OF NOVEMBER ,1982.

ELECTROLYTIC ZINC COMPANY OF
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